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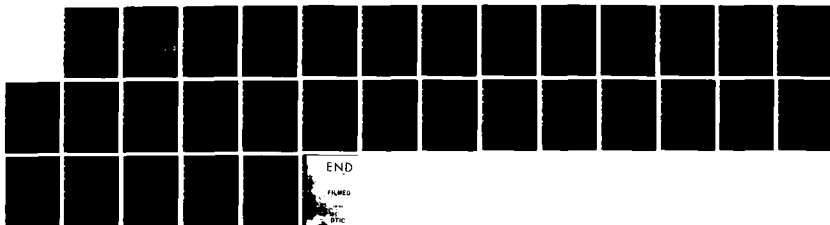
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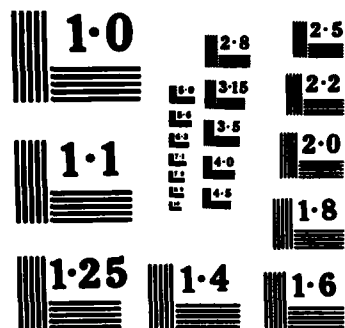
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**Optical Constant Determination
of Thin Polymer Films in the Infrared**

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ABSTRACT

Thin films of poly(vinyl chloride), poly(methyl methacrylate), and poly(styrene) were analysed by Fourier transform infrared spectroscopy. The interference fringes present in the transmission spectra of these samples were used to determine thickness and average refractive index (in non-absorbing regions). Subsequent Kramers-Kronig analysis of these transmission spectra provided the the dispersion of the refractive index and the absorptive index across the entire mid-infrared region. The refractive index and the absorptive index, collectively known as the optical constants, are intrinsic properties of a material, and their spectra are invariant with respect to the geometry and/or thickness of a sample. The intrinsic nature of the derived optical constants was verified by the absence of interference fringes in the optical constant spectra, and by the good agreement obtained between our optical constant spectra and those of other authors.

INTRODUCTION

Classical electromagnetic theory gives an accurate description of the interaction between infrared radiation and matter from a macroscopic point of view. Fortunately, the mathematics of this classical theory is straightforward. Given the optical constants of each homogenous phase and the geometry involved virtually any type of infrared spectroscopic experiment can be mathematically modeled. The optical constants n (refractive index) and k (absorptive index) vary with frequency. This phenomenon, referred to as optical dispersion, depends upon the molecular structure of the material. The optical constants n and k are mutually dependent, and a transformation known as a Kramers-Kronig integral relates them. Thus, before attempting to elucidate molecular information from infrared spectroscopic experiments, one must be aware of the effects of both optical constants on the spectra.

For the analysis of polymers by infrared spectroscopy one is most often interested in absorption. However, various optical effects such as reflective losses and multiple reflections make it impossible to measure true absorption directly. The apparent absorption must be measured, and the true absorption calculated from it in an iterative manner. These calculations, of course, involve the optical constants n and k . The true absorption $A(\nu)$ is related to the absorptive index by the following equation.

$$(1) \quad A(\nu) = 4 \pi k(\nu) \nu d$$

where ν =frequency d =thickness

The difference between the measured apparent absorption and the true absorption can be significant (1-3). For a free standing, thin polymer film the occurrence of interference fringes is especially annoying. For certain cases, the amplitude of these fringes is greater than the peak heights. These

fringes result from multiple reflections between ^{the} interfaces of the polymer film.

Because of the distorting effect of interference fringes on thin film spectra, several different techniques have been devised to experimentally prevent them. These techniques include placing an equivalent cell in the reference beam, sandwiching the sample between infrared windows, roughening the sample surface and tilting the sample at the Brewster angle. The equivalent cell method works to some extent for liquid cell samples, but cannot be used for solid films. Sandwiching the sample between infrared windows does attenuate the fringe level, but the optical contact between plates and sample is often not reproducible. Roughening the sample surface removes interference fringes at the expense of increasing the scattering losses. The Brewster angle method (4) works well, but one must use only polarized radiation at the Brewster angle. The main disadvantage being that orientation measurements can not be made. Furthermore, for this method to successfully remove all the fringes in a spectrum the refractive index must be constant (i.e. no dispersion) across the frequency region of that spectrum.

In addition to the several experimental methods to prevent interference fringes there are several methods to remove them from existing spectra. The method used by Hirschfeld and Mantz (5) uses Fourier transforms, and is especially applicable to FTIR. Since interference fringes are sinusoidal, the Fourier transform of a fringe pattern is a single spike or signature interferogram. Thus, by removing the spike in Fourier space and transforming back to frequency space most of the fringe pattern can be removed. However, it is often difficult to locate the fringe pattern signature (6). Furthermore, there is the problem of how to replace the excised spike. Hirschfeld and Mantz (5) suggested using straight line interpolation between

the ends of the excised segment or using the same region from a separate spectrum of the sample at an angle. Another method proposed by Clark and Moffatt (6) involves subtracting a calculated fringe pattern from the spectrum. This method relies on the subtraction of the quantity $a_1 \cos(a_2 v)$ from the measured absorption spectrum. The parameters a_1 and a_2 are determined empirically. There are problems with this approach, however. The absorption of a spectral band will suppress the multiple reflections that lead to interference fringes. The strength of the absorption and the thickness of the sample determines the amount of fringe attenuation. Thus, subtraction of a sine wave over the entire spectrum will introduce a small amount of error in the band area measurements.

Many researchers have recognized the usefulness of interference fringes for measuring the refractive index and thickness of a sample (7-13). Jones et.al. (7) used the fringe pattern from an empty germanium cell to determine the thickness and wedge parameter of the cell. They then could measure the refractive index of any sample from the fringe pattern of the filled cell. Harrick (8) calculated the refractive index and thickness of thin polymer films by using measurements of fringe spacing at several angles. The fringe spacing increases with increasing angle of incidence(*). Knowing the fringe spacing at two different angles allows one to calculate the refractive index and the thickness. The relationship between the thickness, refractive index and fringe spacing is given by equation (2).

$$(2) \quad d = 1 / (2 n \Delta v \cos \phi)$$

where Δv = fringe spacing n = refractive index
 ϕ = angle of refraction d = thickness

(*) The angle of incidence is defined as the angle the propagation vector makes with the surface normal vector. Thus, a zero angle of incidence indicates that the sample is perpendicular to the beam direction. The plane formed by the propagation vector and the surface normal vector defines the plane of incidence. For zero angle of incidence, the plane of incidence is undefined.

This method is general and can be used for either transmission or reflection spectra. Harrick notes that reflection spectra give a stronger fringe pattern relative to any absorption bands in the spectrum. The accuracy of this method depends upon the accuracy of determining the fringe spacing. This accuracy can be increased by averaging over several fringes, but only if the refractive index is relatively constant over that range. This method should not be applied to a non-isotropic sample which has three distinct, unknown optical axes. In general for an anisotropic sample the refractive index will vary as a function of the angle of incidence. Manifacier et.al. (9) developed a method which includes the effect of weak absorption in the calculations. They used the transmittance values at the maximum and minimum points on the interference fringe pattern to calculate n , k , and d . Their method is a non-iterative simplification of an earlier method developed by Lyshenko and Miloslavskii (14). The inclusion of k in their calculations is significant since weak absorption will affect the amplitude and baseline of the fringes, though a change in k will not alter the fringe position or spacing.

As stated previously, the true absorbance is calculated from the measured, apparent absorbance using the optical constants in an iterative manner. There are many methods of determining the optical dispersion of $n(\nu)$ and $k(\nu)$ from absorption spectra (15-18). One of these methods, Kramers-Kronig analysis, offers several advantages. One measurement (e.g. a transmission spectrum) with a normal absorption infrared spectrophotometer is sufficient to determine both $n(\nu)$ and $k(\nu)$. The Kramers-Kronig relationship itself is a fundamental relationship between $n(\nu)$ and $k(\nu)$, and does not depend on any material constants.

The main source of error with Kramers-Kronig analysis is the limited frequency region over which spectroscopic information is usually available. Equation (3) gives the Kramers-Kronig integral for deriving $n(\nu)$ from $k(\nu)$.

$$(3) \quad n(\nu') = n_{\infty} + \frac{2}{\pi} \int_0^{\infty} k(\nu) \nu / (\nu^2 - \nu'^2) d\nu$$

where: n_{∞} = refractive index at infinite frequency

Note that for each ν' point one integration must be done. At first glance it might seem difficult to apply this equation to real systems. However, closer inspection reveals that absorption bands far removed from ν' will contribute very little to the value of $n(\nu')$. This property allows one to use a finite frequency region for $k(\nu)$ and still obtain accurate values of $n(\nu')$. In practice, for organic compounds in the mid-infrared region a "window" of a hundred wavenumbers on both sides of any absorption bands is usually sufficient for proper analysis of $n(\nu)$. Jones et.al. (19) have discussed the errors involved in using a finite frequency interval and the effect of neglecting neighboring bands. They concluded that a slightly altered form of eq. 3 known as the subtractive Kramers-Kronig procedure produced superior results in error simulation studies. Jezierski et.al. also have analysed the accuracy of the Kramers-Kronig procedure (20).

The n_{∞} constant in eq. 3, in theory, is the refractive index at infinite frequency. In practice, it becomes essentially a scaling constant which compensates for the frequency regions not included in the calculations. Values for n_{∞} can be selected in a variety of ways. Independently measured values of n in or near the frequency region of interest, ATR critical angle measurements, or n values determined from interference fringe analysis all will suffice for n_{∞} values. Jones (23) has noted, that the values of $k(\nu)$ obtained by the Kramers-Kronig procedure are not very sensitive to the value of n_{∞} . Thus, for polymer samples which have refractive indices of 1.4 - 1.5

in non-absorbing regions the n_{∞} value can be estimated (25).

Several authors have applied the Kramers-Kronig analysis method to thin film spectra in the mid-infrared (21-24). Allara et.al. (22) used spectra of poly(methylmethacrylate) supported on NaCl and Si substrates to determine the optical constants of that polymer in the carbonyl stretching region. Jones et.al. (24) determined the optical constants across most of the mid-IR for three different polymers. These polymers were prepared as free standing thin film samples. The thickness was determined by the Harrick method previously mentioned.

We now propose a method to simultaneously remove the interference fringes and determine the thickness and optical constants of a thin polymer sample. The method uses the fringe pattern in a non-absorbing region of the experimental spectrum to measure the thickness and refractive index (n_{∞}). A non-linear least squares procedure is used to determine n_{∞} and d simultaneously from the fringe pattern. This may seem to be improper since only one spectrum is being used to determine two parameters. However, this method uses the fringe spectrum and not just the fringe spacing or fringe position. Intensity information as well as position information is present in the fringe spectrum, and since the refractive index determines the fringe amplitude while the position is determined by the refractive index and the thickness, it is possible to obtain unique n and d values from one fringe spectrum. Using the n and d values obtained from the fringes, Kramers-Kronig analysis is applied to the absorption spectrum to determine the optical constants in an iterative fashion. This method will be applied to simulated spectra first to determine its accuracy, and then it will be applied to real polymer samples.

EXPERIMENTAL

Thin films of poly(methyl methacrylate), poly(styrene), and poly(vinyl chloride) were prepared by solvent casting on glass microscope slides from spectroscopic grade dichloromethane in a solvent vapor saturated environment. The films were subsequently placed in vacuum for 24 hrs. to remove residual solvent. The films were removed from the glass slides by immersing them in distilled water. Only those films which displayed exceptional optical clarity and physical uniformity were used for the infrared analysis.

Spectra were run on a Digilab FTS-20E equipped with a mercury cadmium telluride (MCT) detector at a resolution of 4 cm^{-1} throughout the mid-infrared region. To minimize the effect of any wedging in the sample, the beam size was apertured down to 3 millimeters. Proper baseline determination was important, so the same sample chamber was used to collect both the sample and reference spectra. This procedure eliminates baseline offsets due to small energy differences between the front and back sample chambers.

All computer programs were written in Fortran 77 on a VAX/VMS 11780 system. The Fortran source code for a Levenberg-Marquart non-linear least squares algorithm was obtained from the National Research Council of Canada (26).

THEORY AND CALCULATIONS

The iterative Kramers-Kronig method of optical constant and absolute absorbance determination involves two distinct types of calculations: Kramers-Kronig integration and spectroscopic simulation. First, the measured apparent absorption $A^a(\nu)$, i.e. the experimental absorption spectrum, gives the apparent absorptive index $k^a(\nu)$ (via eq.1). Evaluation of the Kramers-

Kronig integral then gives the apparent refractive index $n^a(\nu)$. These apparent optical constants are then used to calculate or simulate the experimental spectrum. Of course, since the optical constants used for this simulation are not the true values the calculated spectrum will differ from the experimental spectrum. Thus, an iterative approach is necessary. The difference between calculated and observed experimental spectra can be used to refine the values of the apparent absorptive index. A refined value of the apparent refractive index is then calculated by Kramers-Kronig analysis. This whole process is repeated until the difference between the calculated and observed experimental spectra is within acceptable limits.

The apparent optical constants converge to the true values if the sample thickness and refractive index (n_{∞}) have been accurately measured. If either thickness or n_{∞} are not correct the optical constants will not converge to the true values even though the calculated spectrum will converge to the observed experimental spectra. This is true because the calculated spectrum is a function of $n(\nu)$, $k(\nu)$, n_{∞} , and d . For a given n_{∞} and d the solution of an experimental spectrum is unique, however those n_{∞} and d values must be correct to obtain correct $n(\nu)$ and $k(\nu)$.

The algorithm which simulates the spectra of our free standing thin films computes the transmittance and reflectance of each phase present in the experiment. A free standing thin film is a three-phase experiment. This particular algorithm, described by Heavens (27-28), is capable of handling any number of phases. The algorithm assumes that each phase is isotropic and homogenous, and that all interfaces are plane parallel (see fig.1). The optical constants of each phase must be specified, and the thickness of each layer and the angle of incidence must also be given. With reference to figure 1, for a free standing thin film the incident medium is air, the substrate

medium is air, and the single layer is the polymer film. For other samples such as a liquid cell, the walls of the liquid cell would form two additional layers. Allara (22) has used the same algorithm, and he gives a good overview of the mathematics behind it.

The determination of n_0 and d from the fringe pattern by a non-linear least squares method uses the fringe spectrum itself for parameter refinement. Given the fringe spacing and an initial guess for the refractive index, the thickness d is calculated from equation (2). Using n and d the fringe spectrum is then calculated using the spectroscopic simulation model just described. The calculated fringe spectrum is compared with the observed and the n value is adjusted by a Levenberg-Marquart finite difference non-linear least squares algorithm. Unlike the Kramers-Kronig analysis where $n(\nu)$ and $k(\nu)$ are functions of frequency across the entire spectral region, n is assumed constant in these calculations. Therefore it is important to use a narrow frequency region: just large enough to include 1-2 complete fringes. Once an initial refinement using n is complete, a second refinement is performed where n , d , and k are all varied as independent parameters.

RESULTS AND DISCUSSION

Figure 2 shows results from a model simulation. Spectrum 2a is the absorptive index derived from a synthesized spectrum of pure lorentzian peaks located at 1400 cm^{-1} and 1700 cm^{-1} . The refractive index spectrum shown in 2b corresponds to Kramers-Kronig transform of 2a. The dispersion of n in the neighborhood of the absorption bands at 1400 and 1700 cm^{-1} is characteristic. The refractive index always decreases on the high frequency side of an isolated band and increases on the low frequency side. Spectrum 2c is a

simulated thin film absorption spectrum using the optical constants in 2a and 2b. Note the presence of interference fringes. The n_{∞} value for 2b was 1.5 which is typical for polymers. The maximum and minimum values for the optical constants are typical for weak absorption bands of organic materials. Strong bands such as carbonyl stretching modes may have $k(\nu_{max})$ values of 0.4 or more.

Figure 3 shows true absorbance and apparent absorbance and their difference. These spectra were generated using the same optical constants shown in figure 3, but the thickness was changed to 50 microns. The apparent absorption includes the distorting effects of multiple reflections and reflective losses. The difference between the apparent absorption and the true absorption (3c) shows that the interference fringes are attenuated across an absorption band. The degree of this attenuation depends upon the strength of the band. Attenuation of the fringes in regions of absorption occurs because the phase change upon reflection is not 0 or π where k is not zero (*), and because multiple reflections are attenuated by absorption. The dispersion distortion caused by reflective losses for this example is small because the dispersion of n and k is small (weak absorption bands).

To test the validity of determining n_{∞} and d from interference fringes, random noise was added to the model spectrum from figure 2c. The 1200 to 1000 cm^{-1} region of this spectrum was then fit with an initial guess of 1.6 for n . The results of the interference fringe refinement procedure, shown in figure 4 and table 1, indicate that n and d have been accurately calculated. Note that both n and k were included in the calculations, and that this method performed

(*) For k equal zero the phase change upon reflection depends only on the relative magnitudes of n at an interface. This simple mnemonic is helpful. Change in n low to high phase change π , high to low phase change no!

well despite the fact that n and k are not constant (refer to spectra in figs. 2a and 2b).

The n_{∞} and d values determined from the fringes in the $1200\text{--}1000\text{ cm}^{-1}$ region were then used as input for the Kramers-Kronig analysis of spectrum 2c. For comparison purposes the same Kramers-Kronig analysis was repeated with exact values and incorrect values for n_{∞} and d . The absorptive index spectra from these calculations, plotted in figure 5, show that for exact or nearly correct values of n_{∞} and d the Kramers-Kronig iterative procedure will converge to the correct values of the optical constants. The refractive index spectra $n(\nu)$ (not shown) exhibit the same behavior. For spectrum 3d the n_{∞} value was incorrect by only 2% yet the algorithm converged to an obviously wrong value.

Figures 6-8 show free standing thin film spectra of PVC, PMMA, and PS and their optical constants. Analysis of the fringe pattern gave the n_{∞} and d values which were used in the Kramers-Kronig analysis to get $k(\nu)$ and $n(\nu)$. From all three figures it can be seen that the optical constants are fringe free indicating that the calculated d and n_{∞} parameters are accurate. Note that the frequency term in eq. 1 causes the C-H stretching region to lose intensity relative to the fingerprint region for the absorptive index $k(\nu)$ compared to the absorption spectrum $A(\nu)$. Note also the effect of a strong isolated band, such as the carbonyl band (1730 cm^{-1}) of PMMA in figure 7, on the dispersion of the refractive index.

This method of optical constant determination was repeated for samples of the same polymers but with different thicknesses and hence different fringe patterns and peak intensities. Figure 9 shows the results of one such comparison. Only the absorptive index is shown, but the refractive index is

similar. Two completely different sets of calculations were performed on these two samples. The second sample was nearly twice as thick as the first. The absorption spectra from these two samples are very different. Yet, the derived optical constants agree very well.

Another example of the invariant nature of optical constants is shown in figure 10. The data of Allara et.al. (22) for the carbonyl stretching region of poly(methyl methacrylate) is plotted next to our data for the same region. The agreement between the absorptive index spectra is very good. The agreement between the refractive index spectra is also very good on the high frequency side ($> 1732 \text{ cm}^{-1}$) of the spectrum. The disagreement on the low frequency side is partly due to the limited frequency region that Allara et.al. used in their calculations compared to our use of nearly the entire mid-infrared region.

Thus, once the optical constants of a sample have been accurately determined its spectrum in any geometry can be predicted. For polymers various types of infrared spectroscopic experiments such as transmission, external reflection, and attenuated total reflection are used depending upon the sample. The band profiles obtained from these experiments are markedly different, even for the same sample, because each experiment is a complex function of the optical constants and the geometry. To distinguish between spectroscopic changes resulting from true sample differences and those changes due solely to the geometry of the experiment the optical constants must be known. Then the appropriate spectroscopic experiments can be mathematically modeled and comparisons made without regard to sample geometry.

CONCLUSIONS

From the interference fringes in the spectra of thin films of polymers, both the thickness and refractive index (in non-absorbing regions) of the samples were determined simultaneously. Kramers-Kronig analysis of the spectra, using the previously determined n and d , then produced the optical dispersion of the refractive index $n(\nu)$ and absorptive index $k(\nu)$. The derived optical constant spectra were free of interference fringes and other optical distortions which were present in the experimental spectra. Furthermore, our optical constant data for poly(methyl methacrylate) agreed with the data reported by other authors, thus showing the invariant nature of optical constant spectra.

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FIGURE CAPTIONS

1. Mathematical model for spectroscopic simulations. All phases are isotropic and homogenous. Radiation is linearly polarized either parallel (P) or perpendicular (S) to the plane of incidence. I=incident, T=transmitted, R=reflected, n=refractive index, k=absorptive index.
2. Simulated spectrum calculated from given $n(\nu)$ and $k(\nu)$ pair. (A) absorptive index spectrum; (B) refractive index spectrum; (C) Simulated thin film transmission spectrum plotted in absorbance $\{-\log_{10}(I/I_0)\}$; thickness = 30 microns, $n_\infty = 1.5$.
3. Comparison of apparent and true absorption. (A) true absorption spectrum; (B) apparent absorption spectrum; (C) difference spectrum B-A; thickness = 50 microns, $n(\nu)$ and $k(\nu)$ from figure 2. The spectra have been shifted vertically for the purpose of comparison.
4. Observed fringe pattern from figure 2c (noise added) compared with fringe pattern calculated from least squares refinement of refractive index and thickness. Difference spectrum is also shown.
5. Comparison of absorptive index spectra resulting from Kramers-Kronig analysis of figure 2(C) using different estimates of n_∞ and d. The spectra have been shifted vertically for the purpose of comparison. (A) true absorptive index spectrum (figure 2(A)); (B) absorptive index spectrum derived from 2(C) using $n_\infty = 1.50$ and $D = 30.0$ microns; (C) absorptive index spectrum derived from 2(C) using $n_\infty = 1.503$ and $D = 29.97$ microns; (D) absorptive index spectrum derived from 2(C) using $n_\infty = 1.53$ and $D = 30.0$ microns;
6. Experimental thin film transmission spectrum of poly(vinyl chloride) plotted in absorbance $\{-\log_{10}(I/I_0)\}$, and the corresponding absorptive and refractive index spectra. Sample thickness = 3.25 microns, $n_\infty = 1.51$.
7. Experimental thin film transmission spectrum of poly(methyl methacrylate) plotted in absorbance $\{-\log_{10}(I/I_0)\}$, and the corresponding absorptive and refractive index spectra. Sample thickness = 1.45 microns, $n_\infty = 1.43$.
8. Experimental thin film transmission spectrum of poly(styrene) plotted in absorbance $\{-\log_{10}(I/I_0)\}$, and the corresponding absorptive and refractive index spectra. Sample thickness = 2.49 microns, $n_\infty = 1.48$.
9. Comparison of poly(styrene) absorptive index spectra derived from samples of two different thicknesses. (A) thickness = 2.49 microns; (B) thickness = 4.64 microns; (C) difference spectrum A-B. The spectra have been shifted vertically for the purpose of comparison.
10. Comparison of optical constant data from Allara et.al. (ref. 22) with our results. The 1650 to 1800 cm^{-1} region for poly(methyl methacrylate) is shown.

TABLE 1

INITIAL INPUT PARAMETERS			
refractive index = 1.60			
fringe spacing (cm ⁻¹) = 110			
	INITIAL REFINEMENT	FINAL REFINEMENT	TRUE VALUE
REFRACTIVE INDEX	1.517	1.503	$n = 1.500$ $\bar{n} = 1.503$
THICKNESS (MICRONS)	29.56	29.97	30.00
ABSORPTIVE INDEX	-----	0.0002	$\bar{k} = 0.0002$

Results of the least-squares interference fringe refinement procedure applied to the 1200-1000 cm⁻¹ region of the simulated spectrum in figure 2(c). Average values are denoted by \bar{n} and \bar{k} .

FIGURE 1

Mathematical Model of the Optical Experiment

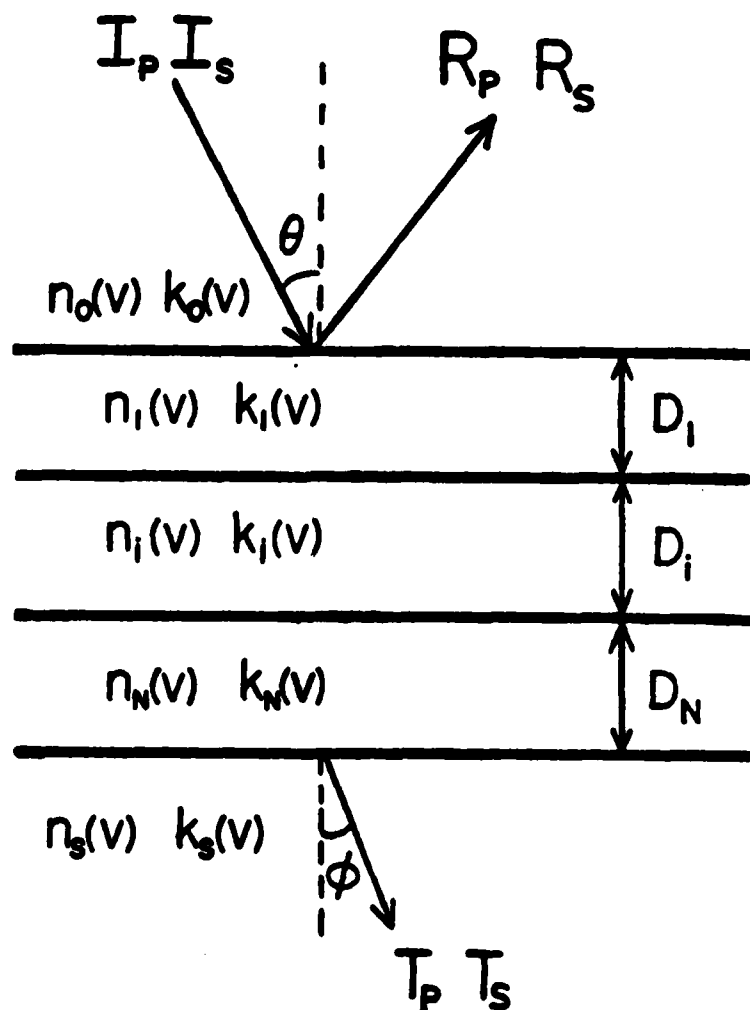


FIGURE 2

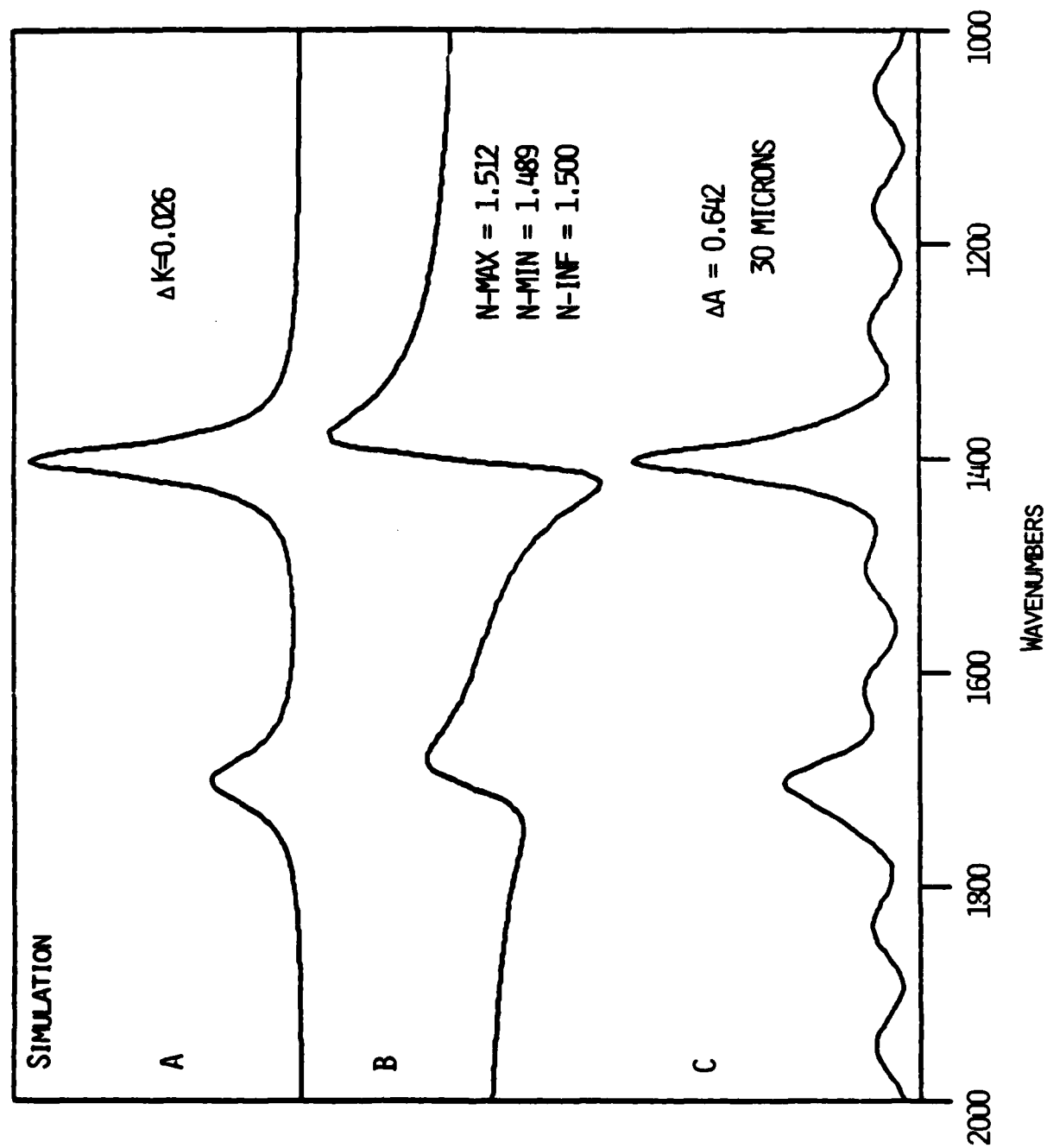


FIGURE 3

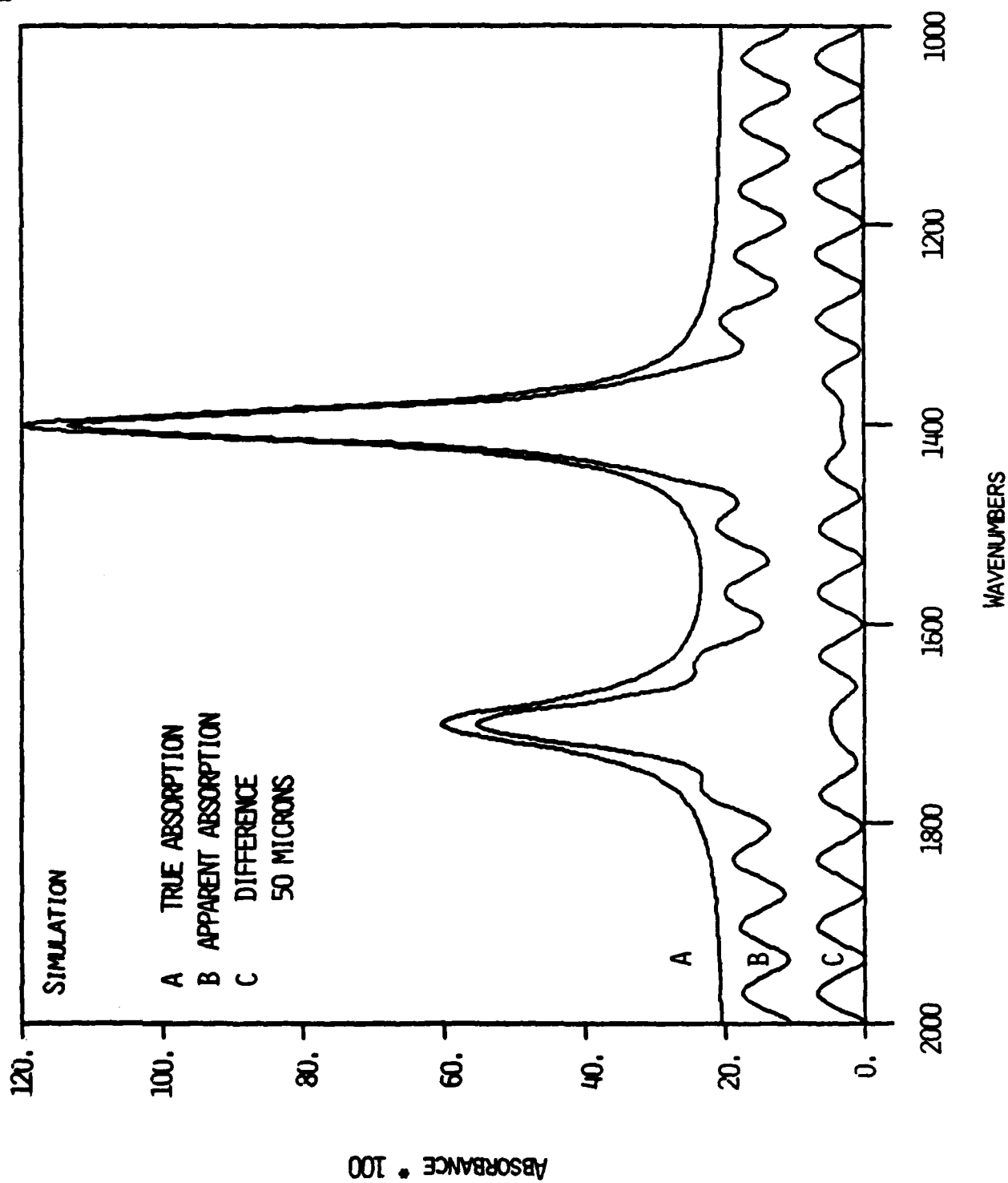


FIGURE 4

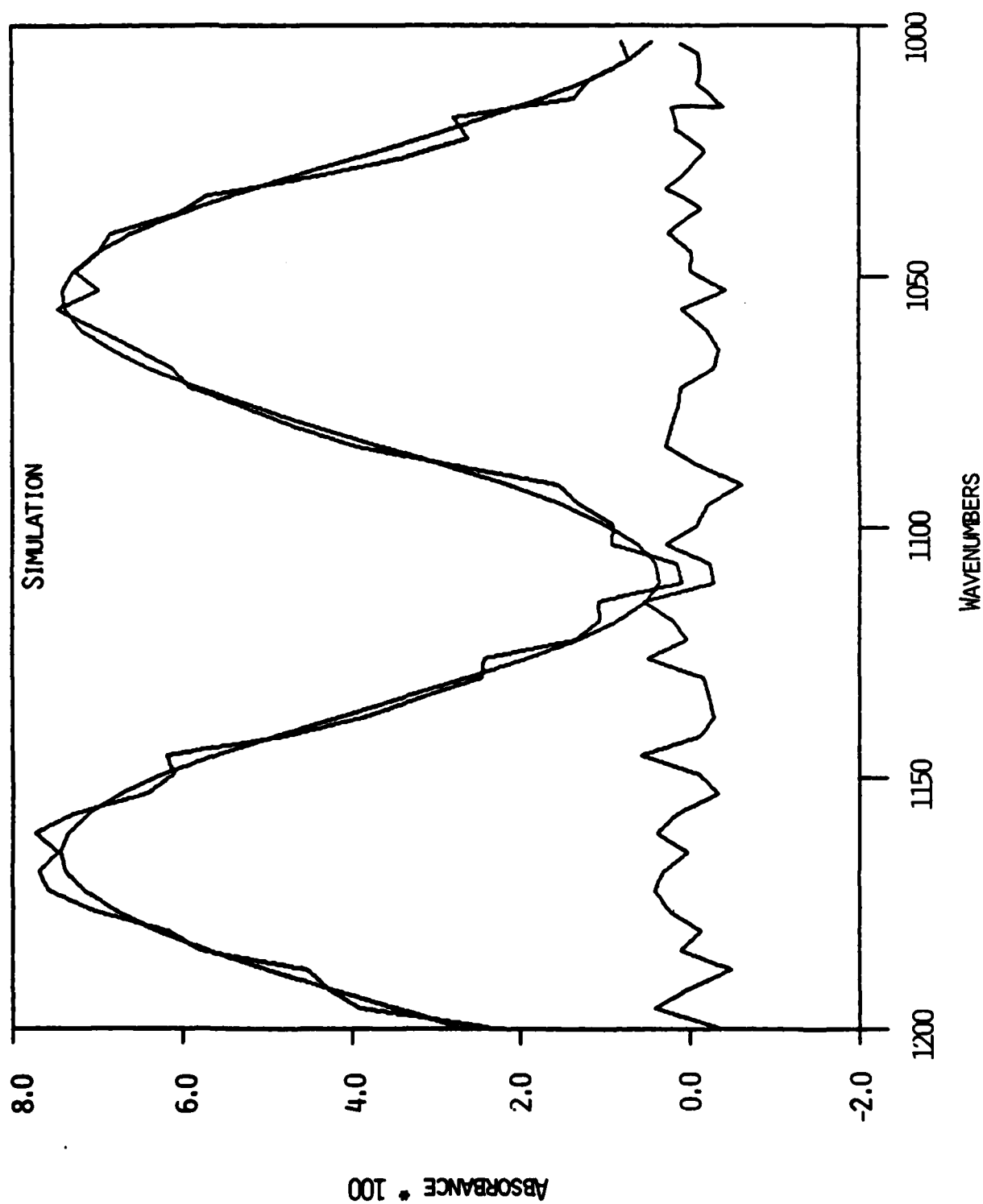


FIGURE 5

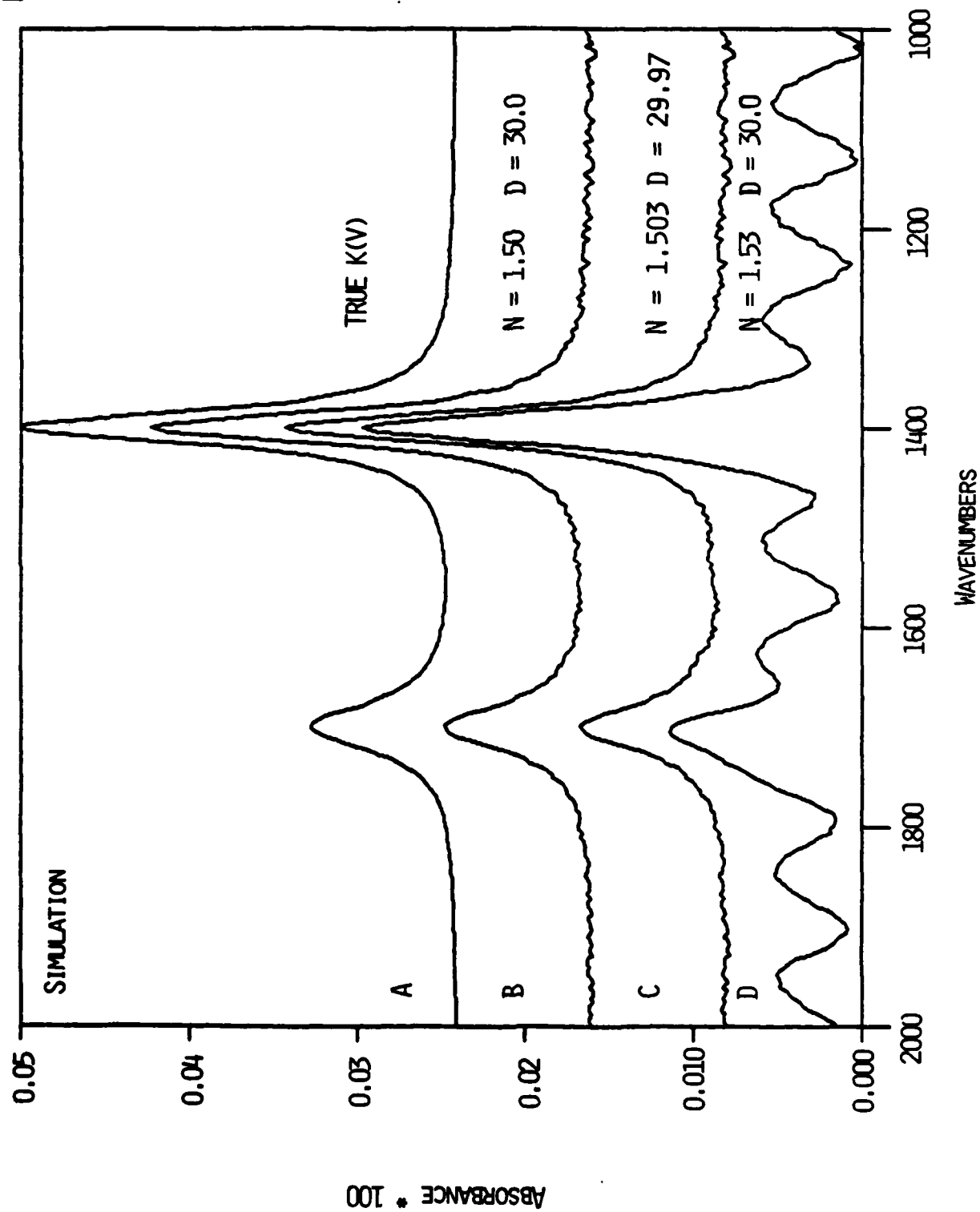


FIGURE 6

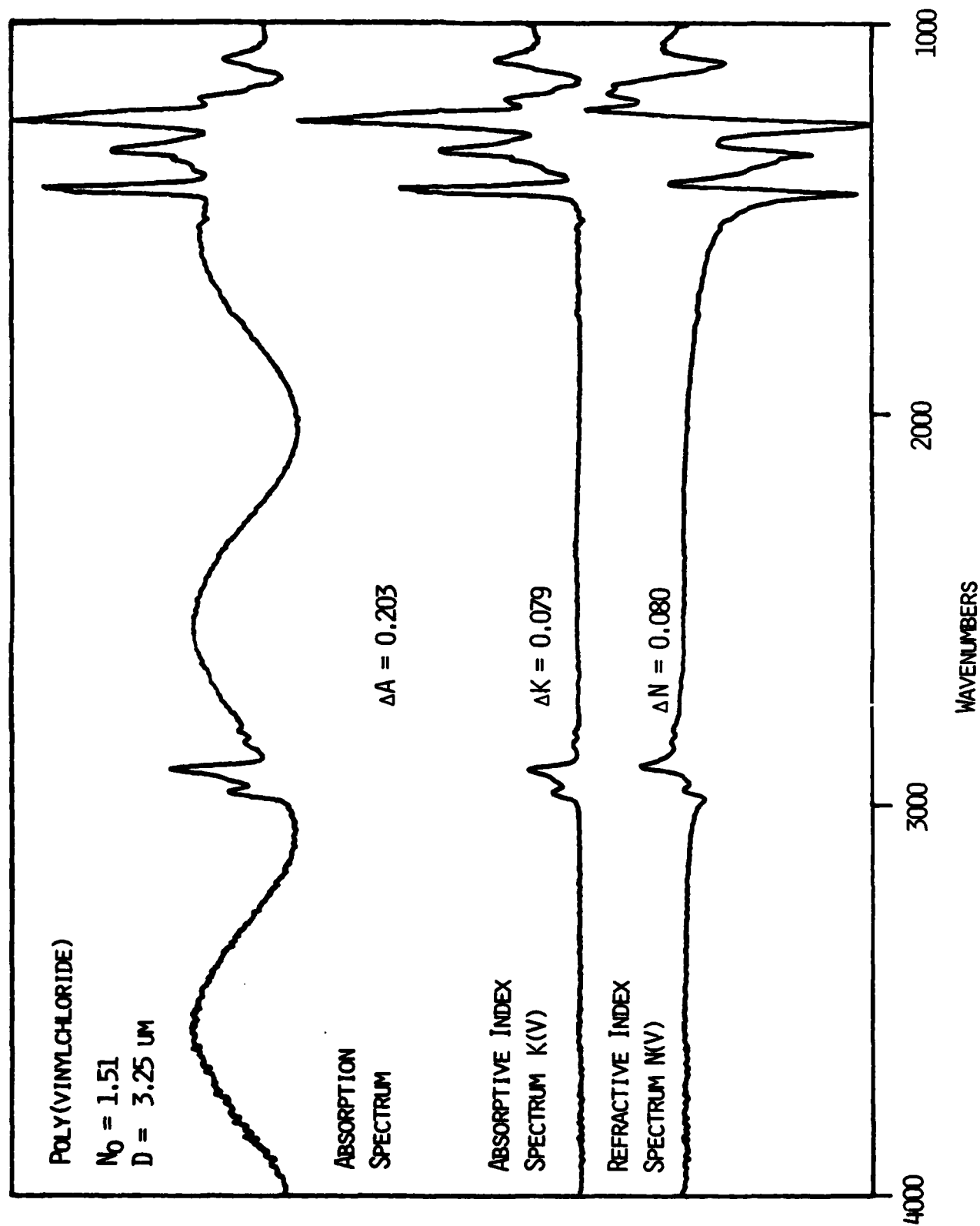


FIGURE 7

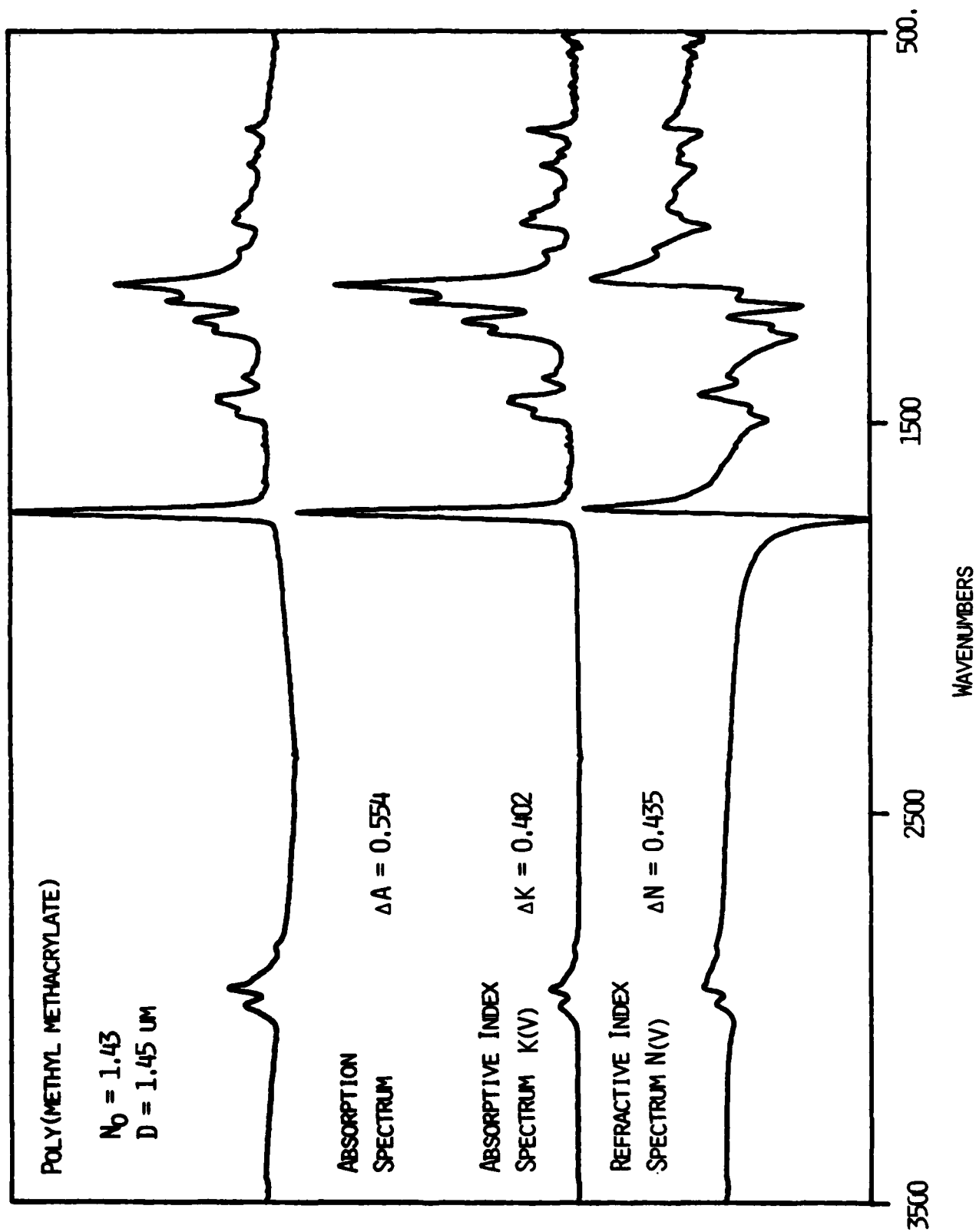


FIGURE 8

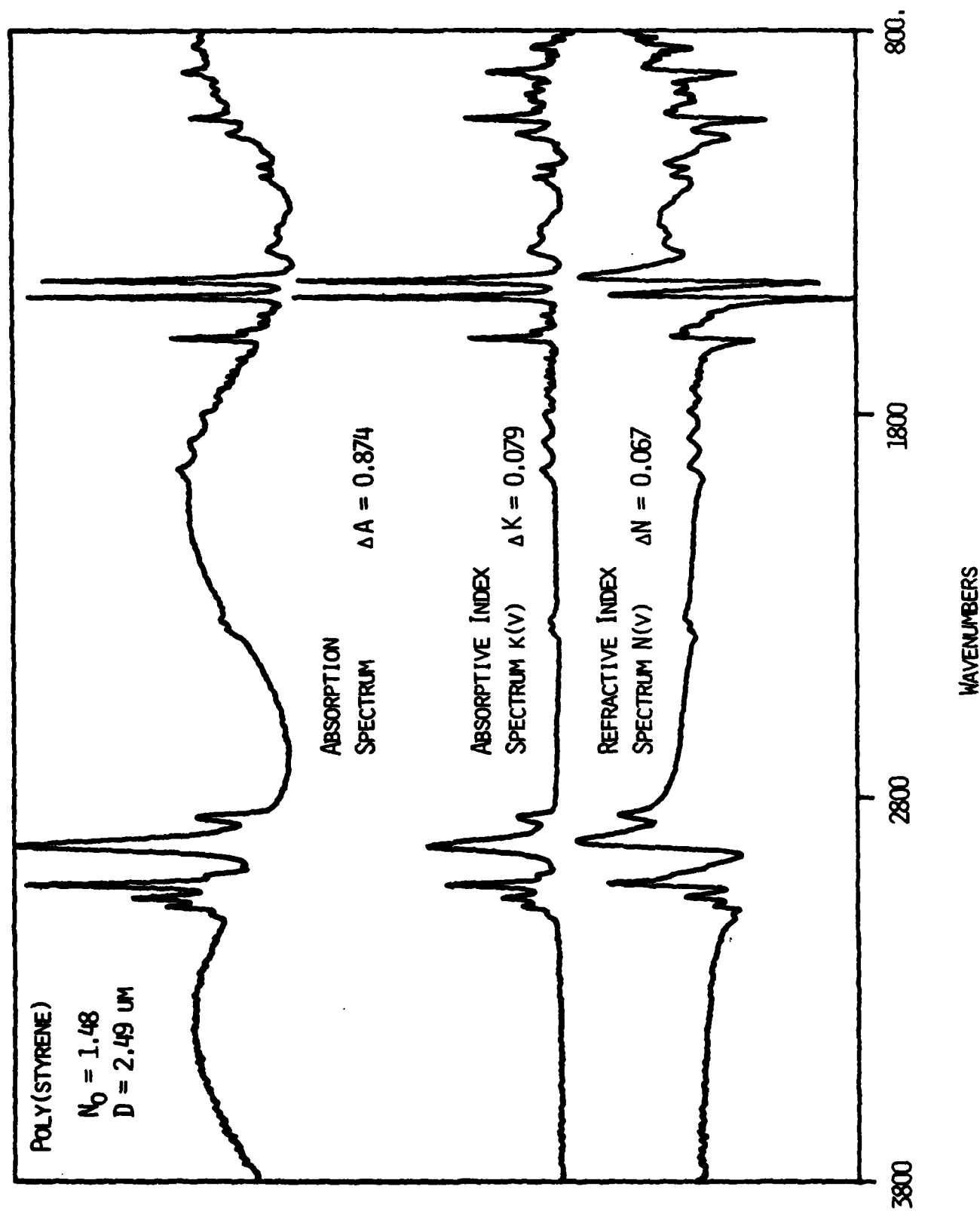


FIGURE 9

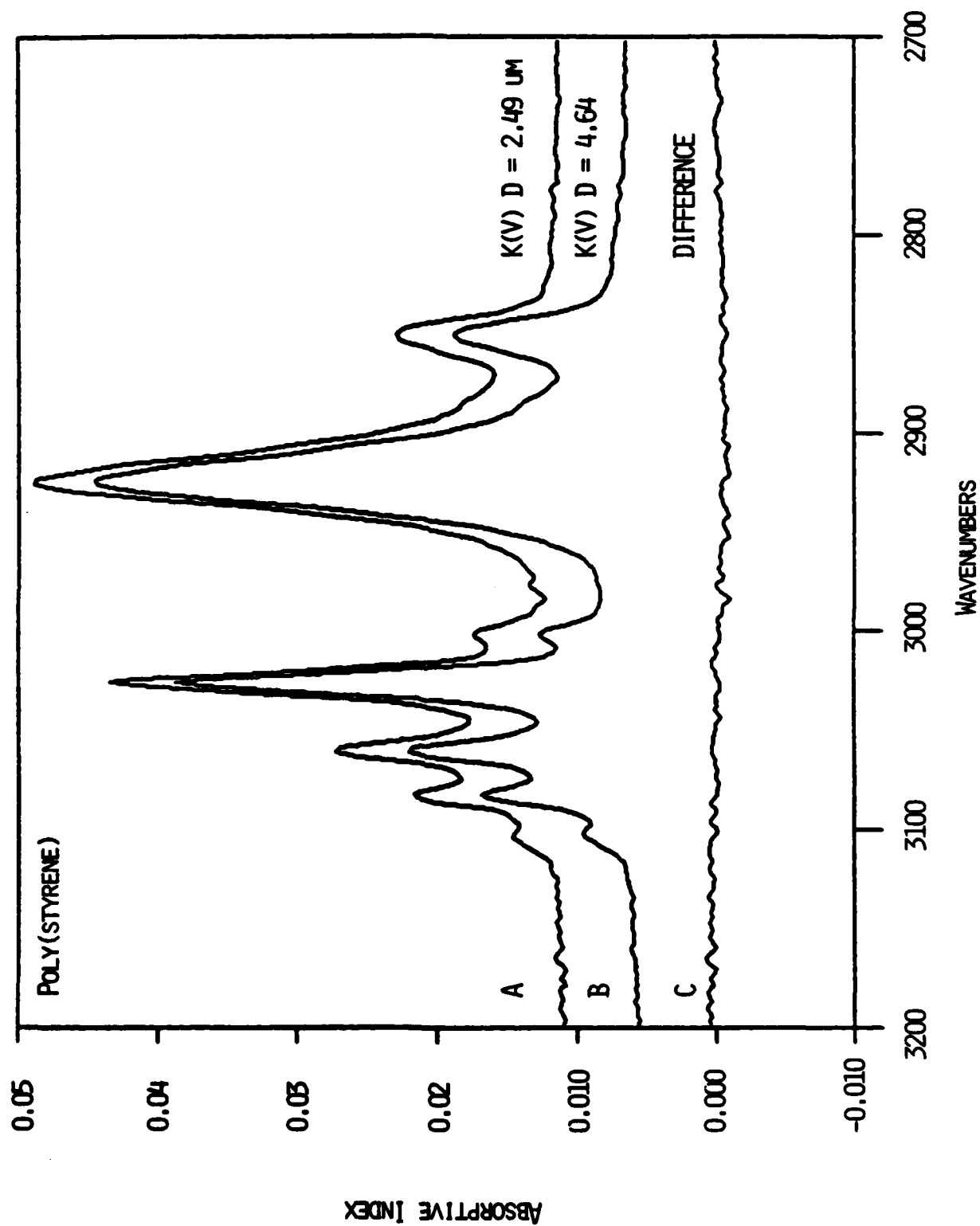
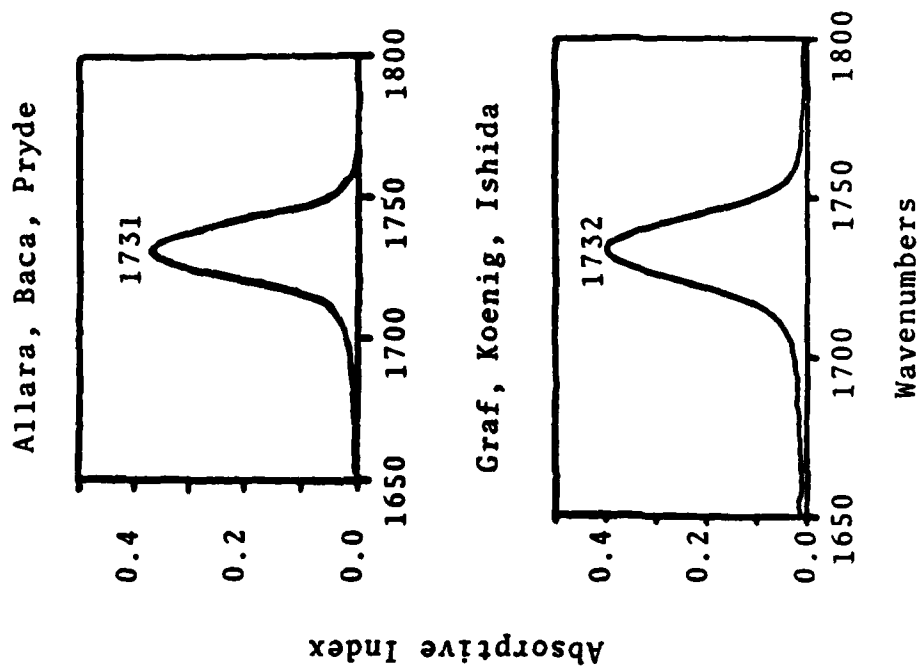
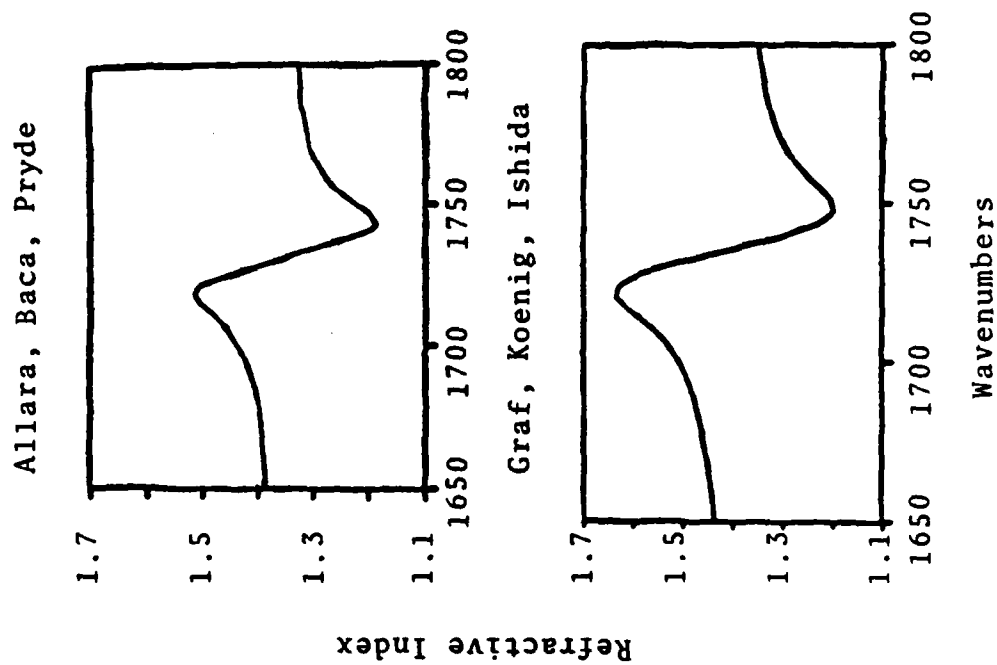


Figure 10



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